Single walled MgF$_2$ nanotubes

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ABSTRACT

We have computer-aided designed $[(\text{MgF}_2)_n]_m$ (with $n = 6, 8, 10, 12, 14, 16, 18, 20, 30$, and $m = 1, 2, 3$) nanotubes. The structural and electronic properties were calculated using the Hartree-Fock and B3LYP methods with the Huzinaga basis set, in order to determine charge, relative energies and optimized structural parameters. The conformational stability was investigated as a function of the unit number along the circumference and the structural parameters. The calculated geometric and electronic properties were compared with available experimental data.

1. Introduction

In recent years, investigation of nanotube materials have resulted in new research areas [1–6], and received significant attention due to their technological applications, e.g., photoluminescence [3,7], semiconductor devices [8], solar cells [8,9], and catalysis [10–12]. In addition to nanotubes other interesting 1D nanostructures similar to nanoribbons and nanobelts have been recently introduced [13–15].

Nanotechnology have developed into a multidisciplinary field during this last decade, including materials science, mechanics, electronics, optics, medicine, plastics, energy and aerospace [16]. 1D nanostructures with different compositions have been synthesized using various methods, e.g., vapor-phase transport process, chemical vapor deposition, arc discharge, laser ablation and template-based methods [16].

In particular carbon nanotubes (CNT) have received considerable interest from condensed matter due to their potential properties for application in nanotechnology [16–19]. Various papers have focused on metals, nitrides, and oxides [20–22]. In particular, the synthesis of inorganic nanotubes similar to fullerenes were investigated, for example, MX$_2$ dichalcogenides (M = Mo, W, Ta, Nb, etc.; and X = S, Se) [2,22]. Patwardhan et al. [23] synthesized hybrid C$_{60}$ fullerene–silica of nanometric size using the functionality of the C$_{60}$ fullerene. The discovery of superconductivity in doped fullerenes has stimulated studies of their electronic structure [24]. Studies were reported regarding the interaction between two C$_{60}$ molecules using MNDO and Hartree-Fock (HF) methods [25] and of the interaction of one or two C$_{60}$ molecules with H, Li, Na and K atoms using the Unrestricted Hartree-Fock (UHF) method [26].

The main goal of this work is to study fluoride systems due to their interesting optical properties [16]. Polycrystalline magnesium fluoride (MgF$_2$) is almost transparent in the infrared (IR) wavelength regime (2–8 μm). MgF$_2$ has optical properties for coating of laser crystals due to its high transmittance and low refractive index ($n \sim 1.38$) [27]. MgF$_2$ has applications for IR windows and coating in optical instruments, space vehicles and frontal domes in heat-seeking missiles. As compared to IR transparent single crystals, polycrystalline MgF$_2$ is relatively simple and inexpensive.
MgF$_2$ and TiO$_2$ both have a tetragonal (rutile) structure with cation coordination number 6 [23].

Although it has been investigated, temperature, structural, optical, mechanical properties and damage resistance of MgF$_2$ coating, it has not been so far well elucidated in the reported literature. The X-ray diffraction analysis is indexed to the corresponding crystal planes of tetragonal (110), (111), (210), (211), (220) and (221) faces [28].

To our knowledge the only available experimental study of MgF$_2$ nanomaterials is from Cao et al. that characterized MgF$_2$ nanomaterials [16]. These samples display rod-like morphology with diameters of 60–100 nm and lengths up to 2 μm. High-resolution transmission electron microscopy (HRTEM) indicates that the nanorod are structurally uniform with an interplanar spacing of about 3.25 Å, which corresponds to the (110) plane of tetragonal MgF$_2$ [16].

Therefore we have studied the electronic and geometric properties of $\{(\text{MgF}_2)_2\}_n^m$ (with $n = 6, 8, 10, 12, 14, 16, 18, 20, 30$, and $m = 1, 2, 3$) nanotubes, where $n$ represents the number of (MgF$_2$) units and $m$ the number of perpendicular unit levels of nanotubes.

2. Computational details

MgF$_2$ stoichiometric nanotubes were computer-aided designed based on the rutile type structure (space group P$_4_2$/mnm) [29] with cell parameters $a = 4.625$ Å and $b = 3.052$ Å [30], while at 0 K the values are $a = 4.615$ Å and $c = 3.043$ Å [31]. The XRD peaks of the tetragonal (110) plane of MgF$_2$ nanomaterials have lattice constants of $a = 4.620$ Å and $b = 3.050$ Å [16] similar to the bulk parameters.

The theoretical growth of these structures were performed using the MgF$_2$ crystalline [110] direction. Cluster model was used for the (MgF$_2$)$_2$ repetition units in order to build the MgF$_2$ nanotubes (Fig. 1).

The full geometry optimization and the periodic conditions case are essential for some electronic and structural properties, due to the presence of dangling bonds in the cluster methodology, but at the same time, this kind of simulations using cluster models is in the state of the art in this area. Therefore, the results of this man-

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\Delta E = E_{\{(\text{MgF}_2)_2\}_n^m} - mE_{\{(\text{MgF}_2)_2\}_{n-1}^m} \quad (m = 2, 3)
\]
Table 1 presents the interatomic bonding distances and the variation of the energy (\(\Delta E\)). The optimized values for the distances using the \textit{ab initio} Hartree-Fock method are \(d_{\text{Mg-Mg}}\) (2.96–2.18 Å), \(d_{\text{F-F}}\) (1.89–2.24 Å) and \(d_{\text{Mg-F}}\) (1.90–2.00 Å), for the nearest atoms. The Mg–F distance is close to the experimental distances of 1.997 and 1.988 Å [29], and magnesium difluoride clusters Mg–F distances between 1.740 and 2.035 Å [34].

All nanotubes show stable energies in relation to \((\text{MgF}_2)_2\) dimer. The variation of the energy, \(\Delta E\) (hartrees) was analyzed using Eq. (2). The variation of energy of nanotube clusters shows some oscillations mainly for the smaller sized nanotubes.

Tables 2–4 show Mulliken charge values and the total dipole moment (Debye). The charges are calculated for each horizontal and vertical planes that are linked perpendicularly for the formation of the m levels of nanotube clusters (see Fig. 2). Only the RHF results are shown for the Mulliken charge. The B3LYP charge values show the same symmetric trend of RHF data.

Table 2 gives values corresponding to clusters with one level (\(m = 1\)). The structures show zero values of Mulliken charge for the horizontal and vertical planes. The nanotubes with two levels (\(m = 2\)) have positive values for the horizontal and vertical planes of the first level and negative values for the planes of the second level (Table 3).

Table 4 shows the nanotubes with three levels (\(m = 3\)). The nanotubes show values equal to zero for the horizontal and vertical planes for the second level, excepting the \(n = 30\) and \(m = 3\)
The nanotubes have values of positive charge for the first level and symmetrically negative for the third level. In general, the uppermost levels of the nanotubes have negative charges due to the high electronegativity of fluorine atoms which are at the end of the nanotube.

The total dipole moment (Debye) increases with the increase of the number of MgF₂ units of the structure. RHF and B3LYP show the same trend for the total dipole moment. All calculated nanotubes at RHF and B3LYP levels present the dipole moment direction depicted on Fig. 1, for the $n = 30, m = 1$ nanotube. The electrostatic potential isosurface is shown on Fig. 4. The horizontal planes have a highly negative potential, mainly due to the fluorine atoms, showing an electron rich region, i.e., the nucleophilic region. The inner fluorine atoms are less negative.

Fig. 5 depicts the Gap (HOMO–LUMO) variation for the studied nanotubes. RHF and B3LYP show the same trend. Otherwise, the B3LYP gap values are smaller than RHF data, which is a known behavior of B3LYP gap. The smallest nanotube with 6 units has a band gap of 8.9 eV and starting from 12 units the band gap converges to a value above 12 eV. The experimental band gap for the crystalline rutile structure is approximately 11 eV at 1528 K [35]. Theoretical values of 10.8 and 6.45 eV have been reported [35].

The HOMO variation as a function of $\left([\text{MgF}_2]_2\right)_n$, units is shown on Fig. 6. B3LYP HOMO values are higher than RHF results. The RHF HOMO converges to $-8.8$ eV as the number of $\left([\text{MgF}_2]_2\right)_n$ units increases. This RHF HOMO value is smaller than the measured first ionization energy of gaseous magnesium difluoride of 13.4 eV [36].

Fig. 7 shows the HOMO and LUMO surfaces. The HOMO is mainly centered on the horizontal planes, where the fluorine atoms have

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**Table 4**

Mulliken charge and total dipole moments for nanotubes of MgF₂ with $m = 3$ levels (in parenthesis the B3LYP values for dipole moments).

<table>
<thead>
<tr>
<th>Nanotubes ($n,m$)</th>
<th>First level</th>
<th>Second level</th>
<th>Third level</th>
<th>Dipole (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Horizontal plane</td>
<td>Vertical plane</td>
<td>Horizontal plane</td>
<td>Vertical plane</td>
</tr>
<tr>
<td>(6,3)</td>
<td>0.07</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(8,3)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(10,3)</td>
<td>0.12</td>
<td>0.12</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(12,3)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(14,3)</td>
<td>0.17</td>
<td>0.17</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(16,3)</td>
<td>0.20</td>
<td>0.20</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(18,3)</td>
<td>0.22</td>
<td>0.22</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(20,3)</td>
<td>0.25</td>
<td>0.25</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(30,3)</td>
<td>0.37</td>
<td>0.37</td>
<td>-0.01</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

**Fig. 4.** Electrostatic potential isosurface for the $n = 8$ and $m = 3$ $\left([\text{MgF}_2]_2\right)_3$ nanotube model.

**Fig. 5.** (HOMO–LUMO) gap energy (eV) for nanotubes of MgF₂.

**Fig. 6.** HOMO energy (eV) for nanotubes of MgF₂.
high available negative charge. The LUMO is more delocalized mainly in the opposite side of HOMO.

4. Conclusions

We have performed RHF and B3LYP calculations of MgF$_2$ nanotubes, with the Huzinaga basis set. Stoichiometric nanotubes were computer-aided designed based on the rutile type structure. The optimized values for the distances using the \textit{ab initio} Hartree-Fock method are $d_{\text{Mg}-\text{Mg}}$ (2.96–3.18 Å), $d_{\text{F}-\text{F}}$ (1.89–2.24 Å) and $d_{\text{Mg}-\text{F}}$ (1.90–2.00 Å).

The nanotubes with $m = 3$ have values of positive charge for the first level and symmetrically negative for the third level. In general, the uppermost levels of the nanotubes have negative charges due to the high electronegativity of fluorine atoms which are at the end of the nanotube. The electrostatic potential isosurface shows that the horizontal planes have a highly negative potential, mainly due to the fluorine atoms, showing an electron rich region, i.e., the nucleophilic region. The smallest nanotube with 6 units has a band gap of 8.9 eV and starting from 12 units the band gap converges to a value above 12 eV.

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References